

APPLICATION FOR UNITED STATES LETTERS PATENT

for

USING SHIFTED SYNGAS TO REGENERATE SCR TYPE CATALYST

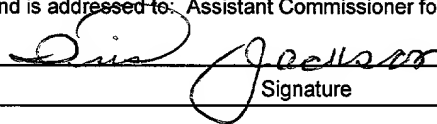
by

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BACKGROUND OF THE INVENTION

Integrated gasification combined cycle (IGCC) power generation systems are used throughout the world to generate power from the gasification of a fuel source. In such systems, a raw synthesis gas (or syngas) fuel gas stream, comprising H_2 , CO, CO_2 , and H_2O , is produced by the partial oxidation reaction of a hydrocarbonaceous fuel with a free-oxygen containing gas, typically in the presence of a temperature moderator such as steam, in a quench gasification reactor.

The syngas produced is cooled by quenching in water to produce a stream of quenched saturated syngas at a temperature typically in the range of about 450°F to 550°F and typically at a pressure of about 700 to 1500 psia. A more detailed description of one such process appears in U.S. Pat. No. 5,345,756.

The syngas produced is then generally cooled to a temperature of 40°F to 140°F and purified in an acid gas removal unit employing a physical or chemical solvent and/or a fixed bed absorption unit to remove impurities, such as H_2S and COS, from the syngas stream. The purified syngas is mixed with a diluent gas, such as nitrogen gas or water vapor, and then fed to the combustor of a gas turbine for power production. The hot combustion gases from the combustor are then sent to an expander/generator that converts the energy released from the combustion gases into electricity. In the combustor, impurities in the syngas produce NO_x and SO_x gases.

An air and nitrogen integrated IGCC system is usually preferred because of the potential for operation at maximum overall efficiency. Air is compressed in a gas turbine air compressor, usually located along the same shaft as the aforementioned combustion gas expander. A portion of compressed air is combusted with the syngas in the gas turbine combustor. The remaining portion, the extracted air, is cooled against the gas turbine diluent stream and fed to an air separation unit (ASU) that provides oxygen to the gasification step and the nitrogen diluent to the gas turbine.

Finally, waste heat from the gas turbine is then commonly used to produce steam, usually in a heat recovery steam generator (HRSG). In the HRSG heat the hot, expanded combustion gases is used to heat a water stream to produce the steam. The produced steam can be used as the temperature moderator in the gasification unit or to superheat the syngas/diluent feed stream to the gas turbine, with the balance of the steam generally

1 used in a steam turbine for further power production. The cooled combustion gases,
2 including the NOx and SOx gases, are then released into the atmosphere, usually through
3 a stack on the HRSG. Various modifications on this general prior art process can be
4 found in U.S. Pat. Nos. 5,715,671, 5,345,756, 5,117,623 and 5,078,752.

5 Gasification is an environmentally clean technology, using many types of low
6 value hydrocarbons to produce the syngas. As environmental laws and regulations
7 become more stringent on the emission of harmful gases, such as NOx and SOx,
8 emissions from gasification plants, particularly IGCC plants, may be required to add best
9 available control technology (BACT) in order to receive environmental permitting.
10 Currently, one BACT process is the process set forth U.S. Patent No. 5,451,558 and
11 continuations thereof. This system uses a catalyst/absorber system to reduce the NOx
12 and SOx emissions in a turbine exhaust gas stream to very low levels, commonly less
13 than 5 ppm, without using ammonia as a reactant. In this process, a turbine exhaust
14 stream is contacted with the catalyst/absorber that oxidizes the nitrogen oxides to
15 nitrogen dioxide; oxidizes carbon monoxide to carbon dioxide; and oxidizes sulfur
16 dioxide to sulfur trioxide. The same catalyst/absorber has a second function of absorbing
17 the oxidized pollutants so that the resultant exhaust gas stream is substantially free of
18 harmful pollutants. This was an improvement over previous selective catalytic reduction
19 (SCR) processes that used hazardous ammonia to lower NOx levels, and then could only
20 lower NOx to the range of 5 to 9 ppm.

21 As described in U.S. Pat. No. 5,599,758, the catalyst/absorber system used to
22 lower NOx and SOx levels can be treated to restore the initial activity or to otherwise
23 substantially improve the activity, by passing a regeneration gas over it. The
24 catalyst/absorber system is contacted with a gaseous stream containing an effectuating
25 amount of reducing agent to remove a portion of the nitrogen oxides. Suitable reducing
26 agents include carbon monoxide, hydrogen and mixtures thereof. The principal
27 component of the gaseous stream is an inert carrier gas such as nitrogen, helium, argon or
28 steam. The reactant gases make up about 500 ppm to 10 percent of the regeneration gas,
29 with the remainder of the regeneration gas being the carrier gas mixture. Several
30 catalyst/absorber beds are used, and are alternated so that regeneration gas is contacted
31 with spent catalyst/absorber beds, leaving the remainder of the beds available to continue

1 to remove contaminants. Thus, the system does not need to be shut down in order to
2 regenerate the catalyst/absorber beds. A process an apparatus for regenerating the catalyst
3 is shown in U.S. Patent No. 5,607,650.

4 Because the '558, '758, and '650 processes reduce NO_x and SO_x emissions from
5 gas turbines, those processes would be desirable for use in the HRSG of an IGCC
6 process. The hydrogen requirements for regenerating the catalyst are generally produced
7 from the autothermal reforming of natural gas. Some IGCC processes, though, are built
8 in areas where natural gas and hydrogen are not readily available. It would be desirable
9 to develop a process that would integrate the IGCC process with the combined '558 and
10 '758 processes, particularly in areas that lack a supply of natural gas and hydrogen.

11 SUMMARY OF THE INVENTION

12 The present invention integrates a gasification unit into a catalyst/absorber
13 process for removing pollutants from the combustion product of a gas turbine. In a
14 preferred embodiment, a small slipstream of syngas from the gasification unit is cleaned
15 in an acid gas removal unit to remove H₂S. The syngas is then processed in a shift unit
16 where the carbon monoxide and any COS present in the syngas are converted into
17 hydrogen, carbon dioxide, and H₂S. The shifted syngas, still containing trace amounts of
18 H₂S, is then processed in a zinc oxide bed, where the trace H₂S is removed. The resultant
19 stream is hydrogen and carbon dioxide rich, making it ideal for use in regenerating the
20 catalyst/absorber system.

21 BRIEF DESCRIPTION OF THE DRAWINGS

22 FIG. 1 illustrates one preferred embodiment of the present invention, wherein a
23 sweet shift process is used to purify the syngas.

24 FIG. 2 shows a second preferred embodiment of the present invention, wherein a
25 sour shift process is used to purify the syngas.

26 DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

27 In the instant invention, carbonaceous fuel is first obtained and prepared for
28 feeding to a gasification reactor. Carbonaceous fuel is any solid, liquid, or gaseous
29 combustible organic material that can be used as feedstock to a gasification process for
30 synthesis gas production. The feedstock for a gasification process is usually a
31 hydrocarbonaceous material, that is, one or more materials, generally organic, which

1 provide a source of hydrogen and carbon for the gasification reaction. The
2 hydrocarbonaceous material can be in a gaseous, liquid or solid state, or in a combination
3 as desired, for example, a solid-liquid composition in a fluidized state.

4 The feed preparation step may not be necessary, given the composition and
5 physical nature of the feedstock. Generally, solid carbonaceous fuels will need to be
6 liquefied with oil or water prior to feeding to the gasifier. Liquid and gaseous
7 carbonaceous fuels may be suitable for direct feed to the gasifier, but can be pre-treated
8 for removal of any impurities that might be present in the feed.

9 The term liquid hydrocarbonaceous fuel as used herein to describe various
10 suitable feedstocks is intended to include pumpable liquid hydrocarbon materials and
11 pumpable liquid slurries of solid carbonaceous materials, and mixtures thereof. For
12 example, pumpable aqueous slurries of solid carbonaceous fuels are suitable feedstocks.
13 In fact, substantially any combustible carbon-containing liquid organic material, or
14 slurries thereof may be included within the definition of the term "liquid
15 hydrocarbonaceous." For example, there are:

16 (1) pumpable slurries of solid carbonaceous fuels, such as coal, particulate carbon,
17 petroleum coke, concentrated sewer sludge, and mixtures thereof, in a vaporizable liquid
18 carrier, such as water, liquid CO₂, liquid hydrocarbon fuel, and mixtures thereof;

19 (2) suitable liquid hydrocarbon fuel feedstocks to the gasifier, is intended to
20 include various materials, such as liquefied petroleum gas, petroleum distillates and
21 residua, gasoline, naphtha, kerosine, crude petroleum, asphalt, gas oil, residual oil, tar
22 sand oil and shale oil, coal derived oil, aromatic hydrocarbons (such as benzene, toluene,
23 xylene fractions), coal tar, cycle gas oil from fluid-catalytic-cracking operations, furfural
24 extract of coker gas oil, and mixtures thereof;

25 (3) also included within the definition of the term liquid hydrocarbonaceous are
26 oxygenated hydrocarbonaceous organic materials including carbohydrates, cellulosic
27 materials, aldehydes, organic acids, alcohols, ketones, oxygenated fuel oil, waste liquids
28 and by-products from chemical processes containing oxygenated hydrocarbonaceous
29 organic materials, and mixtures thereof.

30 Gaseous hydrocarbonaceous fuels that may be burned in the partial oxidation
31 gasifier alone or along with the liquid hydrocarbonaceous fuel includes vaporized liquid

After the feed preparation step, if used, the carbonaceous fuel is sent to a gasification reactor, or gasifier. In the gasifier, the carbonaceous fuel is reacted with a reactive free oxygen-containing gas. The term free-oxygen containing gas as used herein means air, oxygen-enriched air i.e. greater than 21 mole % O₂, and substantially pure oxygen, i.e. greater than about 90% mole oxygen (the remainder usually comprising N₂ and rare gases). Substantially pure oxygen is preferred, such as that that is produced by an air separation unit (ASU). The partial oxidation of the hydrocarbonaceous material is completed, advantageously in the presence of a temperature control moderator such as steam, in a gasification zone to obtain hot synthesis gas, or syngas. Syngas and synthesis gas can and are used interchangeably throughout this specification.

The need for a temperature moderator to control the temperature in the reaction zone of the gas generator depends in general on the carbon-to-hydrogen ratios of the feedstock and the oxygen content of the oxidant stream. A temperature moderator is commonly used with liquid hydrocarbon fuels with substantially pure oxygen. Water or steam is the preferred temperature moderator. Steam may be introduced as a temperature moderator in admixture with either or both reactant streams. Alternatively, the temperature moderator may be introduced into the reaction zone of the gas generator by way of a separate conduit in the feed injector. Other temperature moderators include CO₂-rich gas, nitrogen, and recycled synthesis gas.

A gasification reactor generally comprises a reaction zone, made up of a vertical cylindrically shaped steel pressure vessel lined with refractory, and a quench chamber, such as shown in U.S. Pat. No. 2,809,104, which is incorporated herein by reference. A feed injector, such as shown in U.S. Pat. No. 2,928,460, which is incorporated herein by reference, may be used to introduce the feed streams into the reaction zone. In the reaction zone of a gasifier, the contents will commonly reach temperatures in the range of about 1,700° F (927° C) to 3,000° F (1649° C), and more typically in the range of about 2,000° F (1093° C) to 2,800° F (1538° C). Pressure will typically be in the range of about 1 atmospheres (101 kPa) to about 250 atmospheres (25331 kPa), and more typically in the range of about 15 atmospheres (1520 kPa) to about 150 atmospheres

1 (15,199 kPa), and even more typically in the range of about 60 atmospheres (6080 kPa)
2 to about 80 atmospheres (8106 kPa). See US Patent 3,945,942 describing a partial
3 oxidation feed injector assembly. See US Patent 5,656,044 describing a method and an
4 apparatus for the gasification of organic materials. See also US Patents 5,435,940,
5 4,851,013, and 4,159,238 describing a few of the many gasification processes known in
6 the prior art. The entire disclosures of the above referenced patents are hereby
7 incorporated by reference and relied upon.

8 The hot gasification process product synthesis gas, or syngas, comprises carbon
9 monoxide and hydrogen. Other materials often found in the synthesis gas include
10 hydrogen sulfide, carbon dioxide, ammonia, cyanides, and particulates in the form of
11 carbon and trace metals. The extent of the contaminants in the feed is determined by the
12 type of feed and the particular gasification process utilized as well as the operating
13 conditions. In any event, the removal of these contaminants is preferable to make
14 gasification a viable process, and acid gas (e.g. CO₂ and H₂S) removal is very
15 advantageous.

16 As the synthesis gas is discharged from the gasifier, it passes into the gasification
17 quench chamber for cleaning. The turbulent condition in the quench drum, caused by
18 large volumes of gases bubbling up through the water helps the water to scrub much of
19 the solids from the effluent gas. Large quantities of steam are generated within the
20 quench vessel and saturate the syngas stream. The stream of raw gas is cooled in the
21 quench drum and leaves at a temperature in the range of about 350°F to 600°F (about
22 175°C to 315°C), such as about 450°F to 550°F (about 230°C to 290°C), and a pressure in
23 the range of about 500 to 2500 psia, such as about 1000 psia. Advantageously, fresh
24 quench water is a mixture of make-up water and condensate produced subsequently in the
25 process.

26 The syngas can optionally be subjected to further cooling and cleaning operations
27 involving a scrubbing technique wherein the syngas is introduced into a scrubber and
28 contacted with a water spray which further cools the syngas and removes particulates and
29 ionic constituents from the synthesis gas. The initially cooled gas is then treated to
30 desulfurize the gas prior to utilization of the synthesis gas.

1 The synthesis gas is then sent to an acid gas removal unit so that a substantial
2 portion of the H₂S and other sulfur impurities in the syngas can be removed. The acid
3 gas removal facilities for the synthesis gas, usually employing amine or physical solvents,
4 removes the acid gases, particularly hydrogen sulfide, from the mixed synthesis
5 gas/purge gas stream. The acid gas removal facilities typically operate at low
6 temperatures. After the synthesis gas is cooled to below about 130° C, preferably below
7 about 90° C, the contaminants in the gas, especially sulfur compounds and acid gases,
8 can be readily removed. The synthesis gas is contacted with the solvent in an acid gas
9 removal contactor. The contactor may be of any type known to the art, including trays or
10 a packed column. Operation of such an acid removal contactor is known in the art.
11 Hydrogen sulfide from the acid gas removal unit is usually routed to a sulfur recovery
12 process, with any recovered carbon dioxide being vented to the atmosphere.

13 The syngas can then be utilized for power generation. The syngas is usually
14 superheated, and then combusted. The combusted gas is expanded to produce power by
15 an electric generator driven by an expansion turbine. The heating value and the
16 composition of the syngas is an important consideration when using it for power
17 production. Thus, additional high heating value fuel, such as natural gas, may need to be
18 added to the syngas to increase the heating value of the combustor feed stream.

19 Supplementing the syngas gas turbine fuel with a non-combustible gas heat
20 carrier, or diluent gas, to carry waste heat into the gas turbine will increase gas turbine
21 efficiency. Such non-combustible heat carrier can be a gas such as nitrogen or carbon
22 dioxide, or water vapor either evaporated into the fuel gas in a saturator device or injected
23 directly as steam. The non-combustible gas also provides other benefits such as a
24 lowering of flame temperature and reducing NO_x formation. Due to the introduction of
25 saturated N₂ and saturated fuel gas, the concentration of oxides of nitrogen (NO_x) in the
26 exhaust gas is substantially nil, below 20 ppm (vol) on dry 15% O₂ basis. The nitrogen is
27 usually superheated to a temperature similar to that of the synthesis gas feed to the
28 combustor.

29 Air is also commonly added to the combustor feed stream. The air is compressed
30 by means of a turbocompressor that is driven by the coaxial expansion turbine that, along
31 with the combustor, are the principal parts of the gas turbine. The compressed air enters

1 and NO₂, CO and sulfur dioxide (SO₂). In the catalyst/absorber unit the nitrogen oxides
2 are oxidized to nitrogen dioxide; the carbon monoxides are oxidized to carbon dioxide,
3 and the sulfur dioxide is oxidized to sulfur trioxide (SO₃). This oxidation occurs at
4 temperatures in the range of about 150°F to about 425°F, and more preferably in the range
5 of 175°F to about 400°F, and most preferably in the range of 200°F to about 365°F. The
6 catalyst absorber absorbs the oxidized oxides so that only a small percentage, generally
7 10% or less of the initial oxide pollutants, pass through the system and are released into
8 the atmosphere.

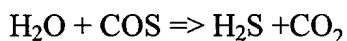
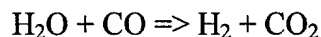
9 The catalyst of the catalyst/absorber unit comprises an oxidation catalyst specie
10 disposed on a high surface area support coated with an absorber material. The oxidation
11 catalyst specie is selected from the group of noble metal elements, base metal transitional
12 elements and combinations thereof. More particularly, the oxidation catalyst species are
13 selected from platinum, palladium, rhodium, cobalt, nickel, iron, copper, molybdenum
14 and mixtures thereof, preferably, platinum and rhodium, and most preferably, platinum.

15 The high surface area support is made of alumina, zirconia, titania, silica or a
16 combination of two or more of these oxides. Preferably, the high surface area support is
17 made of alumina. The high surface area support may be coated on a ceramic or metal
18 matrix structure.

19 The catalyst material is coated with the absorber material. The absorber material
20 is at least one alkali or alkaline earth compound, which can be hydroxide compound,
21 bicarbonate compound, or carbonate compound, or mixtures of hydroxides and/or
22 bicarbonates and/or carbonated compounds. Preferably, the absorber comprises
23 substantially all carbonate, and most preferably sodium carbonate, potassium carbonate
24 or calcium carbonate. The makeup of the catalyst/absorber system is set forth in U.S.
25 Pat. No. 5,451,558, incorporated herein by reference.

26 The absorber ceases to be effective when it becomes at least partially saturated
27 with the oxidized oxides. Specifically, when the level of pollutants emanating from the
28 apparatus after contact with the catalyst absorber increases beyond an acceptable level,
29 the absorber is regenerated using syngas from the gasification unit as the regenerating
30 reducing gas. One preferred embodiment of the present invention involves subjecting a
31 slipstream of syngas produced in the gasification reactor to a sweet shift process. The

syngas is first processed in an acid gas removal unit to remove H₂S from the syngas. This slipstream is preferably removed from the main syngas stream after being processed in the acid gas removal unit described above. The syngas slipstream is then subjected to a shift reactor, where the carbon monoxide in the syngas is converted to carbon dioxide and hydrogen by way of the water gas shift reaction. COS in the syngas is converted into H₂S and CO₂. The synthesis gas from the gasifier is shifted using steam and a suitable catalyst to form hydrogen as shown below:



Alternatively, the syngas slipstream can be subjected to a sour shift process. In the sweet shift process described above, the syngas is first cleaned in an acid gas removal unit before a slipstream of the syngas is processed in the shift unit. In a sour shift process, the shift unit and the acid gas removal unit are switched. A syngas slipstream is taken from the syngas product of the gasifier and sent directly to a sour shift unit. After being processed in the sour shift unit the shifted syngas slipstream is processed in an acid gas unit. The cleaned sour shifted syngas slipstream can then be sent downstream for final preparations for use as the absorber regen gas, or it can be used to produce a purity hydrogen process. Such hydrogen purification processes are known in the art, and include pressure swing adsorption units and membrane separation units. In these hydrogen purification processes a purified hydrogen stream is removed from the syngas, and the remaining portion of the syngas, primarily comprising CO₂, is then sent downstream for final preparations for use as the absorber regen gas.

The shift process (sweet or sour), also called a water gas shift process or steam reforming, is known in the art. The shift process converts water and carbon monoxide to hydrogen and carbon dioxide. The shift process is described in, for example, U.S. Patent No. 5,472,986, the disclosure of which is incorporated herein by reference. Steam reforming is a process of adding water, or using water contained in the gas, and reacting the resulting gas mixture adiabatically over a steam reforming catalyst. The advantages of steam reforming are both an increase the amount of hydrogen and a reduction in the carbon monoxide in the gas mixture.

1 The steam reforming catalyst, or shift catalyst, can be one or more Group VIII
2 metals on a heat resistant support. Conventional random packed ceramic supported
3 catalyst pieces, as used for example in secondary reformers, can be used but, since these
4 apply a significant pressure drop to the gas, it is often advantageous to use a monolithic
5 catalyst having through-passages generally parallel to the direction of reactants flow.

6 The shift reaction is reversible, and lower temperatures favor hydrogen and
7 carbon dioxide formation. However, the reaction rate is slow at low temperatures.
8 Therefore, it is often advantageous to have high temperature and low temperature shift
9 reactions in sequence. The gas temperature in a high temperature shift reaction typically
10 is in the range 350° C to 1050° C. High temperature catalysts are often iron oxide
11 combined with lesser amounts of chromium oxide. Low temperature shift reactors have
12 gas temperatures in the range of about 150° C to 300° C, more typically between about
13 200° C to 250° C. Low temperature shift catalysts are typically copper oxides that may be
14 supported on zinc oxide and alumina. Steam shifting often is accompanied by efficient
15 heat utilization using, for example, product/reactant heat exchangers or steam generators.
16 Such shift reactors are known to the art.

17 After being cleaned in the acid gas removal unit and shifted in the shift unit using
18 either the sweet or sour shift process, the syngas is processed in a final sulfur removal
19 unit which removes the remaining H₂S from the syngas. Preferably, the syngas is
20 processed in a zinc oxide bed. After this final sulfur removal step, the syngas is now
21 ready for use as the regeneration gas in the catalyst/absorber unit.

22 In order to achieve the regeneration the syngas regeneration gas must be contacted
23 with the spent catalyst. Only a portion of the catalyst would need to be regenerated at
24 one time, leaving the remainder to continue to remove the contaminants. Thus
25 catalyst/absorber unit is capable of diverting the exhaust gas from a particular section of
26 the catalyst and to direct the reducing gas thereon. Additionally, the catalyst/absorber
27 allows for the removal of the syngas regeneration gas separately from the turbine exhaust
28 gas exiting the catalyst section. Thus, the HRSG need not be taken off-line to regenerate
29 the catalyst, as simply diverting the turbine exhaust gas to various sections of the
30 catalyst/absorber unit and passing the regeneration gas over the remaining sections allows

for on-line regeneration of the catalyst. A process an apparatus for regenerating the catalyst is shown in U.S. Patent No. 5,607,650, incorporated herein by reference.

Referring now to FIG. 1, a sweet shift process is shown. Hydrocarbonaceous fuels are gasified in gasification reactor 2, and then sent to acid gas removal unit 4 for cleaning. The main portion of the syngas is then sent to combustor 8 of a gas turbine, where it is combusted along with compressed air from compressor 10. The combustion product is then expanded in expander 12 which produces power in generator 13. The expanded combustion gasses are then sent to heat recovery steam generator 14 where the hot gasses are used to produce steam. The combustion gasses are then passed through absorber 16 where they are cleaned prior to being released into the atmosphere. A syngas slipstream for use as the absorber regen gas is removed from the acid gas removal unit 4 product and sent to shift reactor 18. The syngas slipstream is then processed in a final sulfur removal unit 6, preferably a zinc oxide bed. This cleaned syngas slipstream can then be sent to regenerate absorber 16.

Referring now to FIG. 2, a sour shift process is shown. For simplicity sake, the process units from FIG. 1 have retained their original number. Hydrocarbonaceous fuels are gasified in gasification reactor 2, and then the main portion of the syngas is sent to acid gas removal unit 4 for cleaning. The syngas is then sent to combustor 8 of a gas turbine, where it is combusted along with compressed air from compressor 10. The combustion product is then expanded in expander 12 which produces power in generator 13. The expanded combustion gasses are then sent to heat recovery steam generator 14 where the hot gasses are used to produce steam. The combustion gasses are then passed through absorber 16 where they are cleaned prior to being released into the atmosphere. A syngas slipstream for use as the absorber regen gas is removed from the gasification reactor 2 product and sent to shift reactor 18. The syngas slipstream is then processed in an acid gas removal unit 20. The acid gas removal 20 product can then be sent directly to a final sulfur removal unit 6, preferably a zinc oxide bed. Optionally, the acid gas removal 20 product can first be sent to a hydrogen purification unit 22, and then be sent to the final sulfur removal unit 6. After being processed in the final sulfur removal unit 6, the cleaned syngas slipstream can be sent to regenerate absorber 16.

1 While the methods of this invention have been described in terms of preferred
2 embodiments, it will be apparent to those of skill in the art that variations may be applied
3 to the process described herein without departing from the concept and scope of the
4 invention. All such similar substitutes and modifications apparent to those skilled in the
5 art are deemed to be within the scope and concept of the invention.